FURTHER MEASUREMENTS OF THE NEAR IR SPECTRUM OF SHOCK-HEATED AIR

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ABSTRACT

Quantitative spectroscopic measurements have been made of the infrared spectrum of shock-heated air and nitrogen between 0.9 and 1.3 micron. The measurements for air were obtained in the reflected shock region of a shock tube, covering the temperature range 6500-7200° K. The nitrogen data were obtained behind incident shock waves for temperatures between 4600-5700° K, and in the reflected shock region for temperatures from 6800-7500° K. In a previous study it was shown that air radiates much more significantly than nitrogen in this spectral range, and that the radiation could be attributed to transitions between excited electronic states of the nitric oxide molecule. The present measurements confirm these results and also show that the observed excitation energy of the radiation is inconsistent with the energy levels in nitrogen. The data from both studies are reviewed, and it is concluded that the NO hypothesis is consistent with the experimental evidence.

I INTRODUCTION

The earliest measurements of the spectral intensities from strongly heated air in the infrared region of the spectrum were reported by Wentink, Planet, Hammerling, and Kivel[1], who performed experiments between 1 and 5 μ with shock-heated air at 8000° K. They attributed the radiation at wavelengths longer than 2 μ to the continuum resulting from free-free transitions of electrons in the fields of atomic oxygen and nitrogen. Between 1 and 2 μ the continuum was shown to be overlapped by the first positive band system of nitrogen. Subsequent experiments by Keck, Camm, Kivel, and Wentink[2], between 0.7 and 0.9 μ, also performed with shock-heated air, were interpreted to ascribe all of the radiation in this wavelength interval to the N_2 (1+) system. In both cases, however, the measurements were made with insufficient wavelength resolution to permit the identification of the radiating species by means of spectral structure.

The infrared emission spectrum from pure nitrogen was studied at CAL in the course of a research program on detailed, quantitative measurements of the spectral characteristics of air at high temperature. The basic objectives of the research were the determination of the transition probabilities for the pertinent radiating species in air, based on absolute spectral intensity measurements. The results of the nitrogen studies were reported by Wurster[3] in 1962. The spectral characteristics of the N_2 radiation were clearly identified, and the temperature dependence of the radiation shown to correspond to that predicted for nitrogen in thermodynamic equilibrium. However, the measured intensities from pure N_2 were found to be much lower than previously reported values[2] based on air measurements.

Further experiments were subsequently performed to determine the source of the additional radiation from high-temperature air in the infrared wavelength region. It was found that the general magnitude of the measured radiation from air between 0.8 and 0.9 μ was several times greater than could be attributed to N_2. A banded structure throughout the 0.8 - 1.5 μ region was observed, and it was shown by Wurster, Treanor, and Thompson[4] that this radiation could be attributed to transitions between excited electronic states of the nitric oxide molecule.

Wray and Connolly[5] reported the results of subsequent experiments in which the radiation from shock-heated air and nitrogen was measured. In general, their experiments confirmed the CAL results reported in Refs. 3 and 4, and have resolved most of the differences cited by Keck, Allen and Taylor[6], which were based on earlier measurements. In particular, the values for the f number (f_{∞}) of the $N_2(1+)$ system are now in accord, within experimental error, as is the finding that for this band system the electronic transition moment has no measurable variation with internuclear separation. Further, Wray and Connolly verified that the infrared radiation from air exceeded that from pure nitrogen by factors of three to seven. They reported, however, that the excess radiation, i.e., the difference between the measured nitrogen intensities and those in air indicated a better correlation with N_2 than with NO. This would require postulating a mechanism to explain that the $N_2(1+)$ system radiates significantly more when oxygen is present than it does in pure nitrogen. It is concluded in Ref. 5 that while no reasonable explanation could be offered to explain the excess air radiation, some doubt had been case on the NO interpretation of Ref. 4.

Thus, because of the need for an understanding of the infrared spectrum of air, it was decided to reexamine this problem experimentally at CAL in an attempt to resolve the questions that had been raised. The instrumentation was improved and a series of tests made over a broad range of temperature and density in shock-heated nitrogen and air. These present measurements confirm the previous results and provide additional evidence to support the conclusion that electronic transitions in the NO molecule are the chief source of radiation in the near IR spectrum of air at elevated temperatures.

II EXPERIMENTAL APPARATUS

Spectral measurements were made of the radiation behind incident and reflected shock waves in N_2 and air. A filter-photomultiplier combination was used to measure the incident shock wave radiation, while for the reflected shock work, a multi-channel spectrometer was utilized. In order to improve the precision with which the radiation measurements can be obtained, and to extend their total range, considerable effort was expended to improve both the shock tube and the spectroscopic apparatus. For these experiments, use was made again of a high purity, cold-gas driven shock tube, and a 12-channel infrared spectrometer. Although each of these has been described in detail in Ref. 3, the improved setup will be discussed briefly here. The spectrometer is an Ebert-mounted grating instrument which subtends a wavelength range of 0.28 microns in first order, with channel bandwidths of 0.008 microns. This dispersion is usually sufficient

to resolve vibrational band features in the spectra. Behind each of the twelve exit slits is a PbSe detector and associated readout circuitry. Absolute calibrations were made by direct comparison with tungsten filament lamps, which in turn were calibrated against an NBS standard lamp.

Past use of the 12-channel infrared spectrometer has necessitated the use of band-pass limiting filters in the optical train to reduce stray light in the system. In order to achieve a more efficient system, the question of the intensity and origin of the stray light was investigated. It was found to arise from a portion of the dispersed light striking the grating surface, with subsequent scattering through the optical train in the spectrometer. This problem was eliminated by relocating the 12 detectors within the focal plane, and by introducing several stops and baffles, such that no portion of the focal plane overlapped the grating. This resulted in increased astigmatism, which was checked and still found to be negligible for the present application. Several exacting tests were made by using the multichannel spectrometer to measure the known transmittances of a silicon window and of several interference filters. Beyond the cutoff wavelengths of the filters, no signal-above-noise could be recorded, even with very strong incident radiation, and with no band-pass limiting filters. This increased spectral purity of the system, together with new fore-optics and recalibrated standard lamp now make the system especially well suited to quantitative spectroscopic measurements with good wavelength resolution.

The shock tube used in these studies was specifically designed for radiation work[3, 4]. It has a test section 30 ft. long of 3 inches inside diameter with contoured sapphire windows. It is designed for operation at

driver-gas pressures (up to 30,000 psi) and at good purity levels. The test section was thoroughly scrubbed with alcohol and hard-pumped between runs. Ionization gauges have been added to the vacuum system and pressure levels of about 3×10^{-5} torr are maintained in the test section prior to loading of the test gas. The rate of pressure rise of the entire shock tube and gas-handling system was reduced to about 1 μ/hr. In addition, a Baratron differential pressure gauge, capable of measuring pressure in the 0 to 30 torr range with micron precision, was added to the system. It was used to control and measure the initial test gas pressure in the shock tube, and served to make the error in this parameter negligible.

The shock wave speed was monitored over the last 15 feet of the test section with six thin-film heat transfer gauges mounted along the tube wall and an ionization gauge in the reflecting end of the test section. The first four intervals were 3 ft. apart, while the last two intervals near the reflecting wall were 1.5 ft. apart. Megacycle timing counters were used to determine the shock velocity to better than $\pm$ 0.5%. Radiation behind both incident and reflected shock waves was obtained for pure N_2 and dry air, at initial test gas pressures from 1 to 20 torr. The driver gas was room temperature hydrogen at either 2500 or 4000 psi. Repeatability of shock conditions was maintained using the double-diaphragm technique discussed in Ref. 3.

The test gases used in these experiments were supplied by Air Products and Chemicals, Inc., as their ultra-pure, zero gases, with less than 1 ppm. of any specified contaminant. Analyses were procured for the cylinders, which showed each contaminant, as well as total hydrocarbons, to be below 1 ppm. The gases were used without further treatment.

In addition to the 12-channel spectrometer used to monitor the radiation in the reflected shock region, a photomultiplier-filter combination was used to obtain incident shock data approximately 6 ft. from the reflecting end of the shock tube (i.e., 24 feet from the diaphragm). The detector was an uncooled Dumont K1430 photomultiplier used in conjunction with an Optics Technology filter #OTS-706 which peaks at 7100 Å and has a half-width of 200 Å, and a total bandpass of about 1400 Å. After each run the corresponding intensity from a calibrated tungsten lamp was recorded and was used to determine gas emissivity. A schematic of the experimental system is shown in Fig. 1.

The 12-channel spectrometer which was deployed at the reflecting end of the shock tube views a cone-shaped volume of gas (f/6 optics) about one-inch from the end of the shock tube. Each channel obtains a time-resolved intensity record for its particular wavelength bandpass. Again, after each run the radiation intensity from a calibrated tungsten lamp is recorded, and the subsequent ratio of intensities yields the emissivity of the gas directly.

III RESULTS

1. Incident Shock Radiation - Nitrogen

A series of tests was made in pure nitrogen, in which the initial pressures in the shock tube were 1, 3, 5, 7.5, 10, and 20 torr. Typical shock velocities of about 11,000 ft/sec into 20 torr and 15,500 ft/sec into 1 torr were observed at the sidewall monitoring station six feet from the end

of the shock tube. The equilibrium incident shock temperatures obtained ranged from 4600 to 5700° K. Figure 2 shows typical incident shock radiation traces obtained from the photomultiplier-filter combination. At low values of p_1 all of the data showed an overshoot of the radiation at the shock front. As the pressure was increased, however, this radiation overshoot disappeared and at the higher pressures, the radiation seemed to reach a peak near the interface separating the shock-heated nitrogen from the hydrogen driver.

An indication of the heated slug length (i.e., available test time) as the gas passed the sidewall window can also be obtained from the radiation data shown in Fig. 2. For the lowest value of p_1 (1 torr), the available test time 24 feet from the diaphragm is about 60 μ sec, or approximately 40% of the ideal test time based on the equilibrium density ratio across the shock. As the initial pressure is increased, the test time is also increased, such that at p_1 = 5 torr, for example, the measured test time is 140 μ sec, or about 55% of the ideal value. This indicates that for the 3-inch diameter shock tube used in the present investigation an initial pressure of 1 torr shortens the test time considerably, as predicted by Mirels[7]. Figure 3 shows the variation of the measured test time behind the incident shocks as a function of initial pressure.

The intensity obtained from the oscilloscope records was read at the minimum plateau region after the initial overshoot. Assuming that the intensity is proportional to the population of nitrogen molecules in the upper energy levels involved in the transition,

$$I \propto (\rho/\rho)_{N_2} e^{-E/kT} ,$$

a plot of $\ln\left[I/(\rho/\rho_0)_{N_2}\right]$ against $1/T$ should yield a straight line, whose slope is - E/k. These results are shown in Fig. 4, where the best line was drawn through the experimental points, giving an energy of 8.3 eV to the excited state. The bandpass of the detecting system (i.e., a peak at 7100 Å with a half width of 200 Å) encompasses primarily the $\Delta v = 2$ vibrational sequence of the first positive N_2 system ($B^3\Pi - A^3\Sigma$) as seen in the following table[8];

λ (Å)	v', v''
7626.2	3, 1
7503.9	4, 2
7386.6	5, 3
7273.3	6, 4
7164.8	7, 5
7059.0	8, 6
6967.8	9, 7
6875.0	3, 0

For convenient reference, the potential energy curves for N_2 and NO are presented as Figs. 5 and 6, respectively. They are reproduced from a report by Gilmore[9].

The range of vibrational transitions listed above corresponds to energies between 8.0 and 9.0 eV, with 8.3 eV indicating the $v' = 5$ transition. Thus, it may be concluded that the recorded radiation is, in fact, from these transitions in nitrogen. Because of the low resolution of the filter-photomultiplier detector combination, however, no attempt was made to deduce an f-number from these data.

2. Incident Shock Radiation - Air

A similar series of tests was made in dry air, with the same initial pressures as the nitrogen series. Here, typical shock velocities of 11,450 ft/sec into 20 torr and 15,520 ft/sec into 1 torr were observed at the sidewall monitoring station. The equilibrium incident shock temperatures ranged from 3800 to 5000° K. Typical incident shock radiation traces are shown in Fig. 7 for these air runs. Again, the initial radiation overshoot is very apparent at p_1 = 1 torr, but rapidly disappears as p_1 is increased. The available test time behind the incident shock wave can also be determined from these records and representative data are included in Fig. 3 for the air runs. At p_1 = 1 torr, for example, the experimentally determined test time is about 55 μ sec, or 35% of the ideal test time based on the equilibrium shock density ratio. This time increases at the higher values of p_1 and at 10 torr, Δt = 120 μ sec, or about 55% of the ideal test time 24 feet from the diaphragm.

The radiation data were again read in the plateau region of each oscilloscope trace. The intensity data showed no correlation with the nitrogen content of the air. In addition, there was no correlation with the NO concentration. The scatter for the air data is much larger than that for the nitrogen results, and no meaningful excitation energy could be obtained for either attempted correlation. One complication in these tests is that in this temperature range it is possible that other species, radiating within the bandpass of the detecting system, may be contributing to the measured intensity. Thus, such results are not too unlikely because of the limited reliability that can be placed in broad-band filter techniques for quantitative

spectral measurements. This is particularly true for multicomponent gases, where spectral resolution of the spectrum is required to determine the origin of the measured radiation. No further attempt was made to treat these incident shock data; rather, the bulk of the effort was concentrated on the reflected shock work with the multichannel spectrometer.

3. Reflected Shock Radiation - Nitrogen

Coincident with the incident shock measurements, the 12-channel infrared spectrometer was used to monitor the radiation in the reflected shock region, where the equilibrium temperature ranged from 6800-7500° K. The purpose of this series of runs was to obtain new measurements to compare with the data reported in Ref. 3. A set of data obtained with the 12-channel spectrometer for a single run is shown in Fig. 8 with the wavelength corresponding to the center of the 0.008 μ bandpass noted for each channel. All of the nitrogen reflected shock data resembled those shown in Fig. 8, which illustrate the onset of radiation due to the passage of the reflected shock past the viewing port and a gradual rise toward a plateau region, where the intensity levels were read. It was found that this radiation is generally terminated by an abrupt decrease or increase of the radiation depending upon the run conditions. The useable test time was defined from the records as corresponding to the time from onset of radiation to the end of the plateau. This test time, Δt, which varied from about 80 μ sec for $p_1 = 1$ torr, to approximately 180 μ sec for the $p_1 = 20$ torr runs, is shown in Fig. 9 for both driver pressures used. It may be noted that, in general, the available reflected-shock test times are about 20% greater than the test times measured for the incident shocks.

The general nature of the spectrum obtained can be seen in Fig. 10 for three different test conditions, and agrees well with the results shown in Ref. 3, where calculated intensity distributions are shown. Excitation energies were obtained at the three wavelengths chosen for the subsequent air spectrum analysis, i.e., 1.03 μ (channel 11), 1.13 μ (channel 7), and 1.21 μ (channel 4). This was done by plotting $\ln\left[I/(\rho/\rho_0)_{N_2}\right]$ vs $1/T$ as discussed earlier and using the best straight line through the data. These curves are presented in Fig. 11. For λ = 1.21 and 1.03 μ, the lines drawn through the data correspond to excitation energies of 7.4 eV, the energy of the upper level of the transition ($B^3\pi$, $v'=0$) in nitrogen (see Fig. 5). At λ = 1.13 μ, however, the line shown yields an energy of 8.6 eV, corresponding to $v'=6$, which is too high to contribute substantially to the radiation at this wavelength. Other possible radiators at this wavelength, viz., the N_2^+ Meinel system, or the CN red system as discussed in Ref. 3, involve transitions to the ground state, and hence have very low excitation energies. However, the actual 12-channel records, shown in Fig. 8 also indicate a different radiation history for channels 7 and 8, which are located near this wavelength region, indicating the possibility of another radiating source. This point is at present unresolved.

4. Reflected Shock Radiation - Air

An extensive series of measurements was undertaken for air in the reflected shock region, with equilibrium temperatures ranging from 6500-7200° K. The purpose of this set of experiments was to determine the radiating species and energy of the excited state. Figure 12 shows a set of the 12-channel data for a single air run. Reflected shock test times

for the air runs ranged from about 40 μ sec at p_1 = 1 torr to 110 μ sec at p_1 = 10 torr. These are also shown in Fig. 9. For air, the reflected and incident shock test times were comparable.

The general nature of the spectra obtained from shock-heated air is shown in Fig. 13, where four representative spectra are shown for different conditions of temperature and density. The interlacing of points at given gas conditions was achieved by rotating the grating, which effectively moves the spectrum along the 12 exit slits of the spectrometer. Since the coverage of the spectrum is not continuous, the data essentially constitute bar graphs of intensities averaged over the bandpass. The connecting lines are used to guide the eye and cannot be taken to represent intensities between the points. It was from a series of such spectra that excitation energy determinations were made.

The experimental scatter in the data can be seen in Fig. 14, where the results are shown for a series of runs designed to produce the same temperature and density. The data spread is due to the reading of intensities from the run and calibration records, and to the variations in gas conditions imposed by the $\pm$ 1/2% wavespeed measurement. The largest spread of points can be seen to be contained in a $\pm$ 10% bracket. The unusually high spike at 1.22 micron was seen in the air runs, but not in the pure nitrogen cases. Its sharpness suggests that it is an atomic line, although it has not been identified. This feature is further discussed in Section IV.

The runs were made over the broadest range of temperature and density that could be accommodated by the apparatus. A range of 6500 to 7200° K in temperature corresponded to partial density variations of a

factor of 25 in NO and 10 in N_2. The limitations were set by the signal-to-noise ratio in recording the intensities at low temperatures, and by the shock tube capability at high temperatures. Unfortunately, the lower gas density at higher temperatures precluded the use of higher wavelength resolution due to lack of radiated intensity. Thus, identification of the radiating species by structured features in the spectrum could not be accomplished. A discussion of these features and their comparison with published data was presented in Ref. 4.

Three wavelengths within the prominent peaks of the air spectrum were chosen (1.03, 1.13, and 1.21 μ) for which the excitation energy of the radiation was obtained. The radiation data were correlated assuming the radiation to arise from N_2, and then from NO, as discussed earlier in Refs. 4 and 5. Also, for the NO correlation, corrections were made for the small amount of radiation contributed by N_2, as based on pure N_2 measurements. The resultant graphs are shown in Figs. 15-17.

A cursory examination of the graphs indicates, at first, a possible correlation with either N_2 or NO. However, three significant features can be readily observed. The first is the considerably improved correlation when the radiation is scaled by the NO partial density, rather than by N_2. The second feature is that the smaller data spread makes it possible to obtain a better linear variation using the NO correlation. Even accepting the greater scatter for the N_2 curves, the best lines that can be passed through the points all correspond to energies that lie between 3 and 5 eV. These energy values are below even the level of the $A^3\Sigma$ state of the nitrogen molecule (see Fig. 5). Even if a mechanism could be devised to

explain why nitrogen radiates more strongly in the presence of oxygen than in a pure nitrogen environment, the lack of the correct excitation energy obtained from the experiments still poses a serious question. These considerations, therefore, rule out nitrogen as a radiating source. The third feature of Figs. 15-17 is that there is no systematic dependence of the NO-correlated radiation on the initial pressure in the shock tube. All three of the above features are in disagreement with the stated conclusions in Ref. 5.

IV DISCUSSION

The present series of experiments, both in nitrogen and air, was undertaken for the purpose of obtaining more definitive data on the radiating species in shock-heated air in the infrared portion of the spectrum. The results of this work will now be discussed in conjunction with those of Ref. 4 to give a consistent picture of the experimental results obtained at CAL for infrared air radiation.

Using the improved instrumentation in the present series, the previous results of Ref. 4 in both pure N_2 and air were quantitatively reaffirmed. The data again show that radiation from air at elevated temperatures (5000-7000° K) in the infrared between 0.9 and 1.3 μ is significantly more intense than can be attributed to the nitrogen concentration, based on intensity measurements in pure N_2. The earlier experiments in pure nitrogen and pure oxygen have shown that the presence of both species is required to produce the recorded spectrum. Impurity effects in those

experiments were discounted, since the same results were obtained with both commercial air and premixed samples of pure nitrogen and oxygen.

By varying the ratio of N_2 to NO over a broad range in the shock-heated test gas, it was reported in Ref. 4 that at 5000° K, the radiation in the prominent peak at 1.04 μ correlated with the partial density of NO. For example, the radiated intensity could be changed by a factor of 30 for the same concentration of N_2, by changing the amount of NO in the heated test gas. The results obtained from the present experiments are consistent with this NO interpretation. A large number of tests yielded resolved spectra of air radiation in the infrared in the region behind a reflected shock wave. Using three wavelengths (1.03, 1.13, and 1.21 μ), an attempt was made to correlate the radiation intensity with either N_2 or NO. As discussed earlier, Figs. 15-17 indicate a definite correlation with the NO concentration. Even accepting the considerable scatter present in the N_2-normalized data, the best slope yields an excitation energy that is much too low to be compatible with the picture of N_2 as the source of the radiation.

The excitation energies derived on the basis of NO normalization are:

λ (μ)	E (eV)
1.03	7.2 ± 0.7
1.13	8.7 ± 1.0
1.21	6.7 ± 0.6

The error estimates were simply obtained by determining the extremes of possible straight lines drawn through the points. It can be seen that the method lacks sufficient precision to permit a correlation with particular electronic states of NO. However, the energies obtained fall within values

consistent with these states, (see Fig. 6) and offer no conflict with the NO hypothesis.

An interesting feature of the comparison of the present results with those of the previous work (Ref. 4) concerns the sharp spike at 1.22μ which was mentioned earlier. One unresolved point in the original NO work was the low (5.2 ± 0.5 eV) excitation energy for the radiation at 1.219 μ. This energy is below that which can be attributed to electronic states of NO. However, with the higher resolution of the present experiments, the spike is clearly delineated from the broad maximum in the spectral structure (Figs. 13 and 14) and for the present analysis, the intensities at 1.21 μ were used to deduce the excitation energy listed in the table above. However, if the intensity of the 1.22 μ spike is normalized by the NO concentration, the new data again yields a low value of 5.5 eV.

Thus, the question posed in Ref. 4 concerning the low excitation energy appears to be resolved by the presence of the sharp spike in the spectrum. In an attempt to determine its origin, runs were made in pure N_2 at the same wavelength setting. As can be seen in Fig. 10, however, the spike was not observed. Likewise, no explanation could be obtained by considering atomic oxygen as a possible radiating source. To date, no further attempts have been made to establish the origin of this radiation.

The pure nitrogen measurements discussed in this report showed a consistent correlation for both the incident and reflected shock cases. However, when air was used as the test gas, no correlation of the recorded intensities could be made with either NO or N_2 for the incident shock. It is assumed that this is due to the poor spectral definition resulting from the

use of a relatively wide band-pass filter photomultiplier detector for the incident shock measurements. This points up the need for adequate spectral resolution for quantitative spectroscopic studies of complex gases.

The conclusions discussed above may be contrasted with those reported by Wray and Connolly in Ref. 5, which were based upon measurements made in air and nitrogen, but for incident shock waves only. Further, the measurements were made at only two wavelength intervals, 0.72 and 1.04 μ, and hence were unable to show spectral structure, which aids in species identification and permits discrimination against possible contaminant radiation superimposed on the recorded spectra.

While there is general agreement in the measurements and in the conclusion that air radiates more strongly than nitrogen in the infrared, there are also several significant differences. The present results were all found to be independent of the initial pressure in the shock tube, as should be the case. This is at variance with the data shown in Ref. 5, which indicate an unexplained pressure dependence of the nitrogen f number measurement at 0.72 μ, and also show a pressure dependence in the results when the air radiation is correlated with NO. Thus, while this air radiation was shown to correlate more favorably with N_2, the present air data are shown to correlate with NO.

The discrepancy arising in the comparison of the results of the present experiments with those of Ref. 5 may be due to differences in the operating characteristics and limitations of the shock tubes used for the different experiments. The experimental data reported in Ref. 5 were obtained in a pyrex shock tube having a test section of 1.5 inch internal

diameter and a length of 10 feet, with the radiation measurements made approximately 9 feet from the diaphragm station. Since all measurements were made behind incident shock waves, and require the attainment of gas-dynamic equilibrium in the available test time, it is pertinent to estimate this test time at a point 9 feet from the diaphragm. This can be done by first computing the ideal test time for equilibrium flow conditions. Due to mixing and diffusion at the hot gas-driver interface, this full ideal test time is never realized in actual shock tube experiments. It was shown in Section III that roughly 1/3 to 1/2 of this ideal time was obtainable in the shock tube used for the present experiments. At low values of p_1($\sim$ 1 torr), a 1.5 inch diameter shock tube would operate even less efficiently than one having an inside diameter of 3 inches, where only 1/3 of the ideal test time was observed. It is estimated that for a point 9 feet from the diaphragm, the probable test times for incident shock wave air measurements would be:

p_1 torr	T_2(°K)	Ideal Test Time (μ sec)	Approx. Actual Test time (μ sec)
1	5000	60	60 x 1/2 $\approx$ 15-20
1	6000	38	38 x 1/3 $\approx$ 10-13
5	5000	64	64 x 1/2 $\approx$ 30
5	6000	50	50 x 1/2 $\approx$ 25

Thus, extremely short test times are involved, especially for the p_1 = 1 torr case. A study of the figures given in Ref. 5 indicates that the argument for the observed p_1 dependence in the NO correlation is based primarily on the 1 torr data for both wavelengths discussed, 0.72 and 1.04 μ.

An examination of the incident shock traces for both air and N_2 in Figs. 2 and 7 of the present reports show that for p_1 = 1 torr, there is an

extreme overshoot in the recorded intensity at the shock front. This peak decays in a time approximately equal to the test times shown in the preceding table for a station 9 feet from the diaphragm. Unfortunately, no actual data records are given in Ref. 5 to indicate whether or not the overshoot mentioned in that text has fully decayed in the available test times, and how the equilibrium radiation levels were determined. However, as reported recently by Wray[10], for a different series of experiments using the same shock tube and optical arrangement, an incident shock radiation record is given for pure N_2 at p_1 = 1 torr. The shock speed is 4.56 mm/μ sec, giving an equilibrium temperature of about 5500° K. The data record shows an overshoot peak which has not fully decayed to a level plateau as long as 18 μ sec after the initial shock passage.

If the 1 torr data were to be discounted based on the above discussion, the data obtained at higher pressures does not then show a pressure dependence in the NO correlation. For both wavelengths reported in Ref. 5, the scatter is large, and in fact slightly larger for the N_2 correlation than for the correlation with NO. It may also be noted that using the 1 torr data, an activation energy of 7.4 eV was obtained for both the NO and N_2 curves at 0.72 μ. Based on the wavelength table and results discussed in Section III of this report, an energy of about 8.5 eV is required to identify the proper radiating state of N_2 at this wavelength.

In light of the above discussion, it seems that the incident shock measurements of Ref. 5 are inconclusive in defining the source of infrared radiation in shock heated air.

V CONCLUSIONS

Based on the measurements described in this report and the previous results of Ref. 4 which have been summarized, it is concluded that NO is the dominant source of infrared radiation from equilibrated air in the 5000-7000° K temperature region.

The inherent capability of the shock-tube in terms of the maximum density of air that could be attained at the higher temperatures of the present experiments set the limitation on the radiation intensities that could be generated. Unfortunately, these intensities did not permit consideration of experiments with higher spectral dispersion. Also, the finite range of temperature limited the precision with which the excitation energies of the states could be determined. Coupled with the complex arrangement of the relevant electronic states in NO, this did not permit a correlation of spectral features with the identification of the states involved.

At present the spectral distribution of the infrared radiation from heated air cannot be determined theoretically. However, such predictions can be made by scaling the experimental data of Fig. 13 according to the concentration of NO and using the measured temperature dependence of the spectral prominences.

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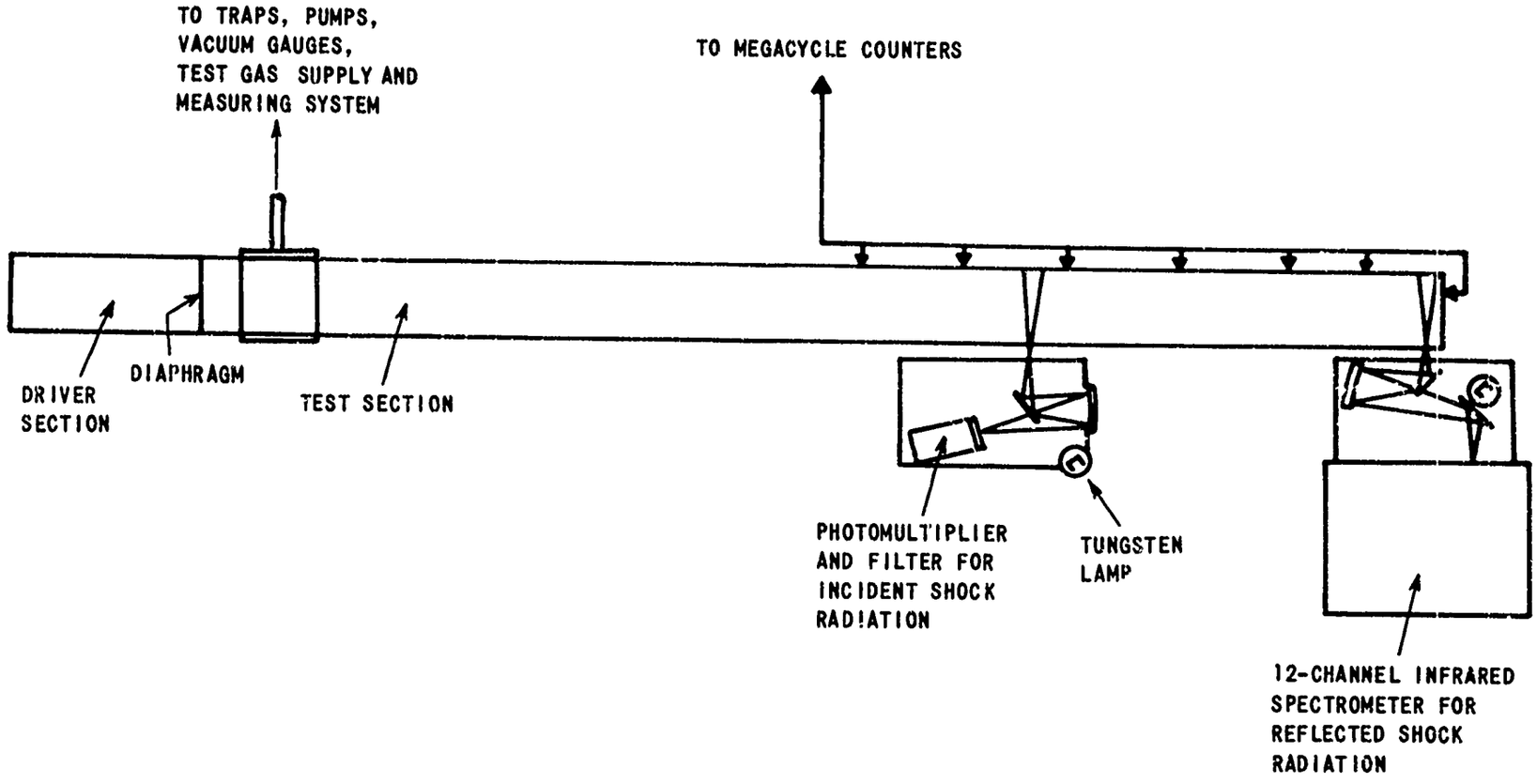
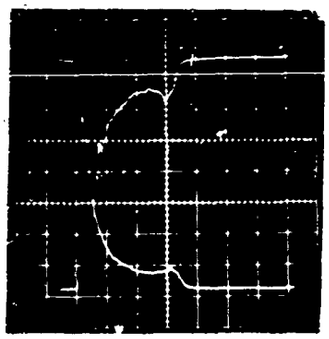
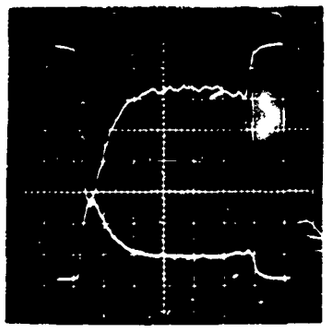


Figure 1 SCHEMATIC OF EXPERIMENTAL APPARATUS

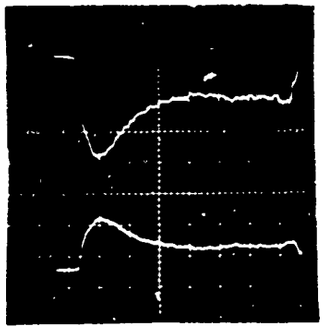


t → ⟷ 20 μSEC

P_1 = 1 TORR
U_S = 15,590 FT/SEC



P_1 = 3 TORR
U_S = 13,870 FT/SEC



P_1 = 5 TORR
U_S = 12,990 FT/SEC

Figure 2 RADIATION PROFILES BEHIND INCIDENT SHOCK WAVES IN NITROGEN ($\lambda \sim 7100$ Å)

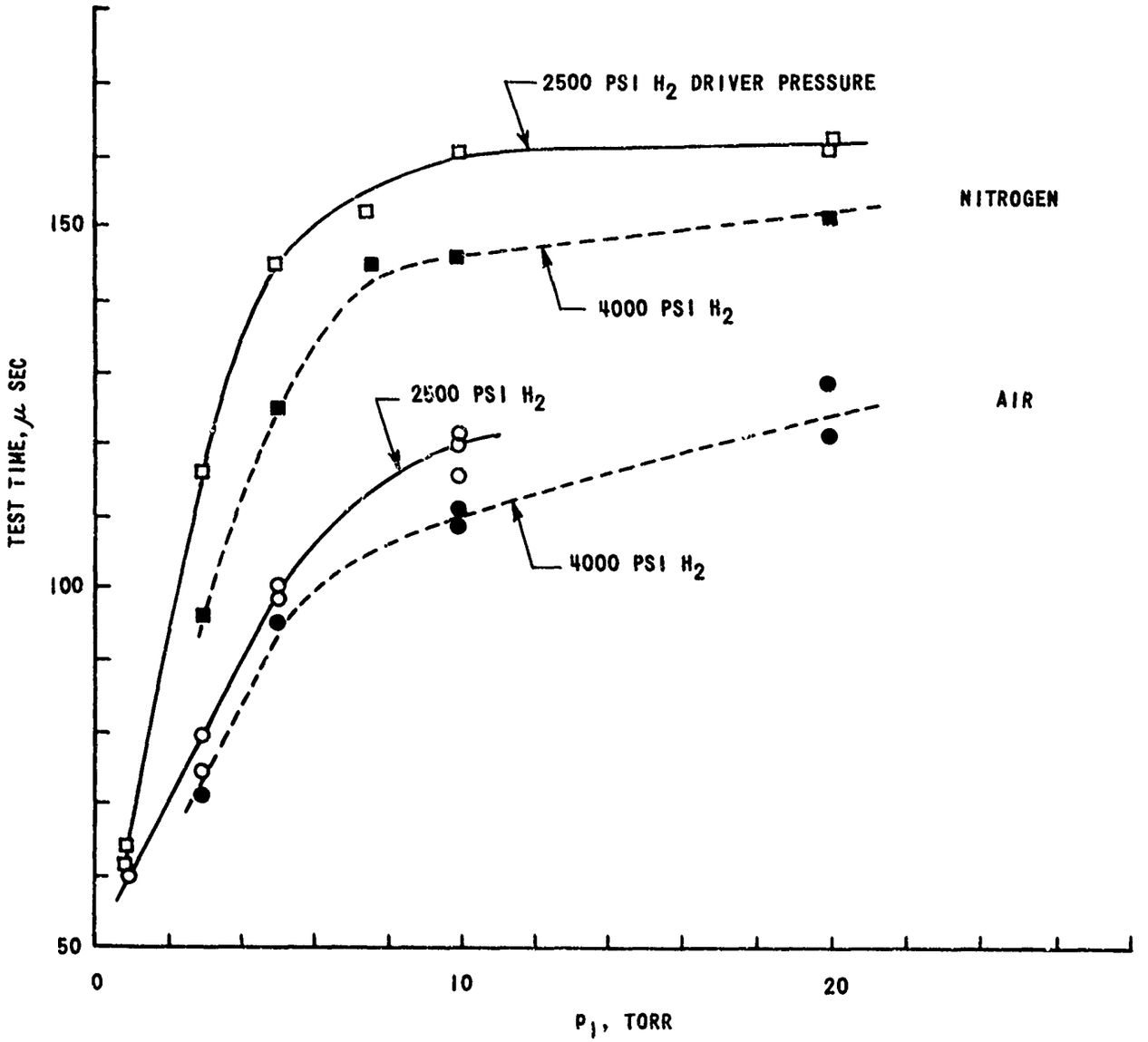


Figure 3 TEST TIME BEHIND INCIDENT SHOCK WAVES, 24 FEET FROM DIAPHRAGM

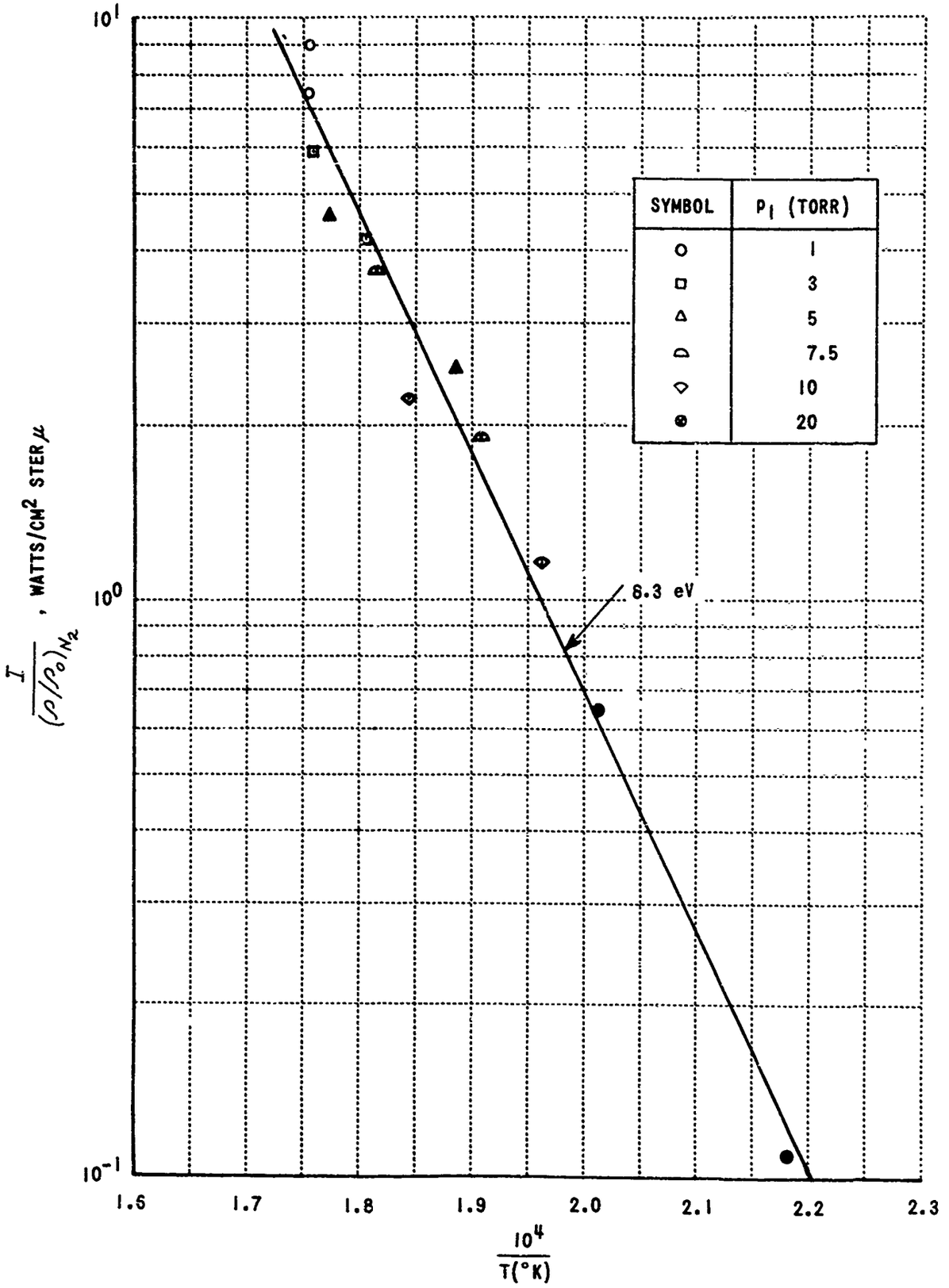


Figure 4 TEMPERATURE DEPENDENCE OF THE INCIDENT SHOCK NITROGEN RADIATION

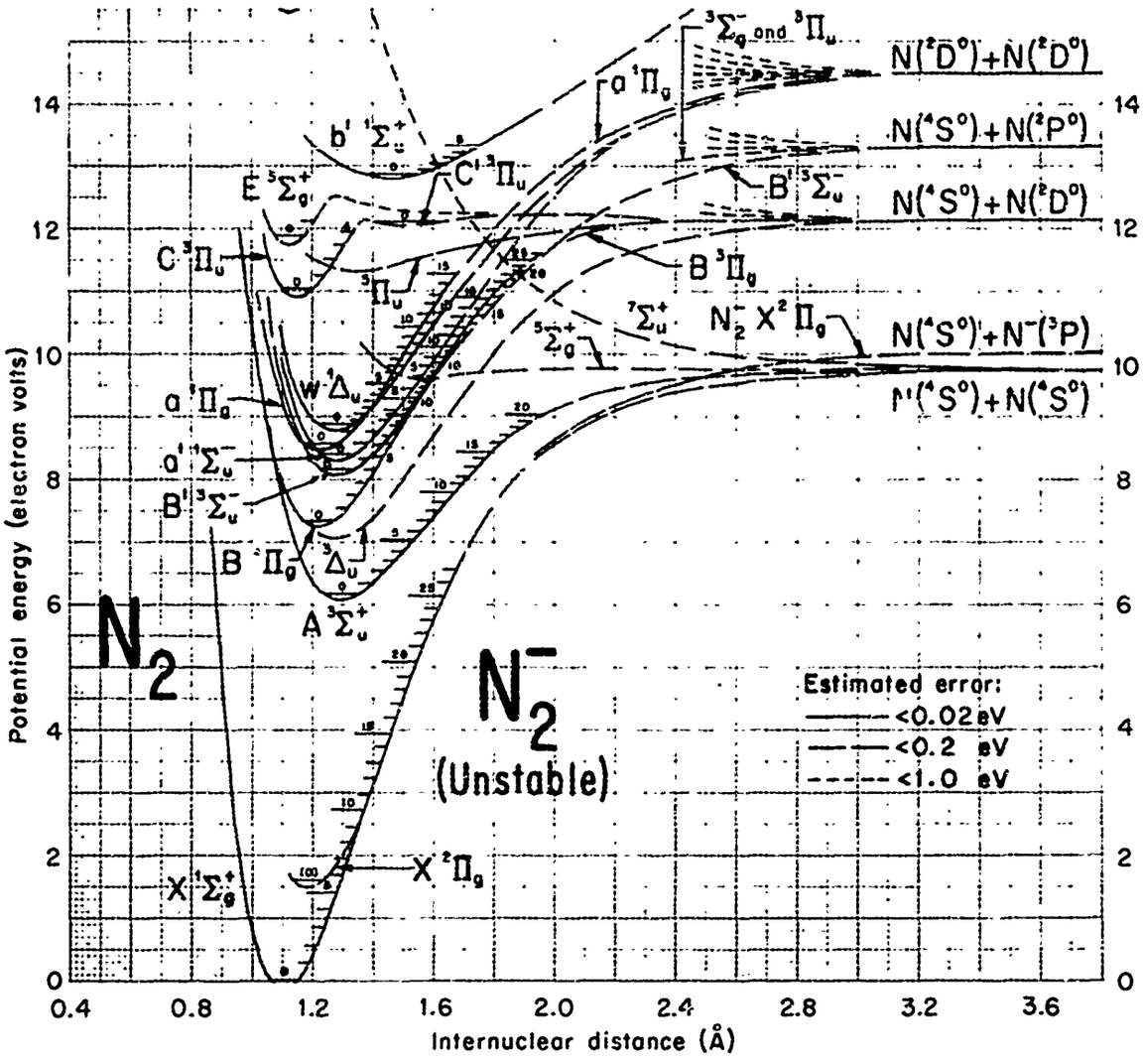


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Figure 5 POTENTIAL ENERGY CURVES FOR N_2^-,(UNSTABLE) AND N_2

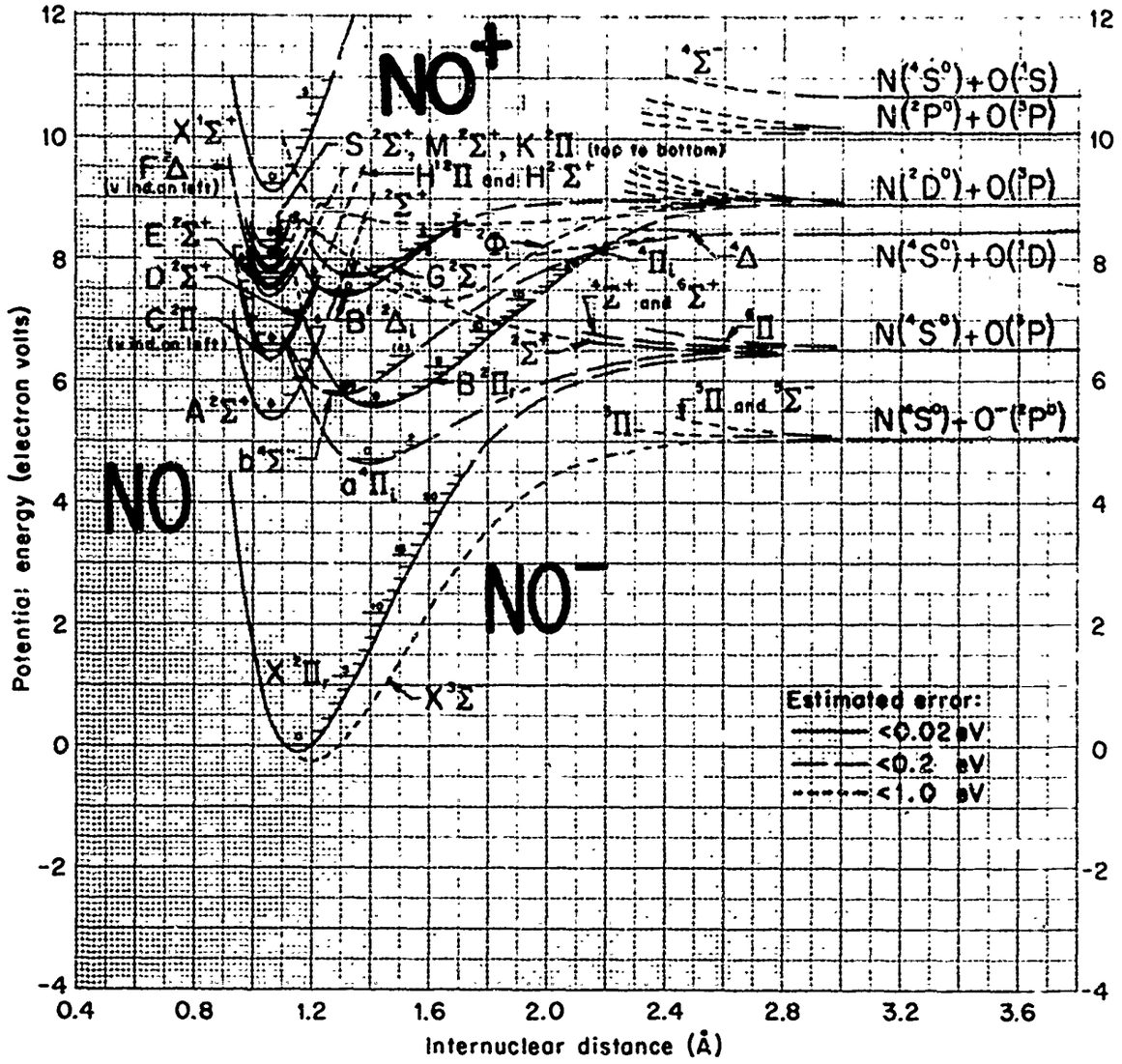

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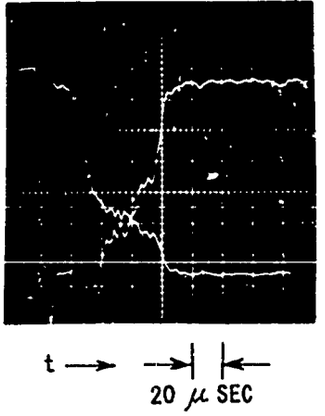
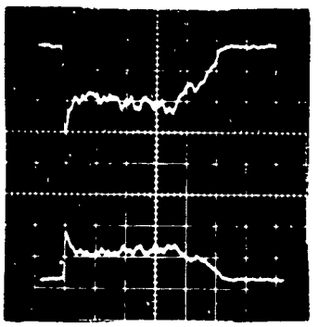
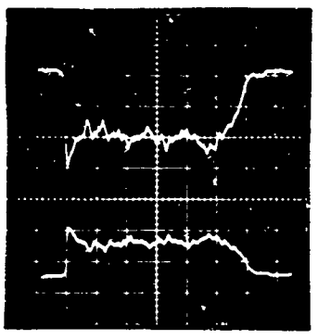
Figure 6 POTENTIAL ENERGY CURVES FOR NO⁻, NO AND NO⁺



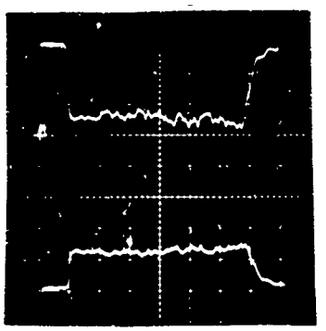
p_1 = 1 TORR
U_S = 15,520 FT/SEC



p_1 = 3 TORR
U_S = 13,900 FT/SEC



p_1 = 5 TORR
U_S = 13,130 FT/SEC



p_1 = 10 TORR
U_S = 11,960 FT/SEC

Figure 7 RADIATION PROFILES BEHIND INCIDENT SHOCK WAVES IN AIR ($\lambda \sim$ 7100 Å)

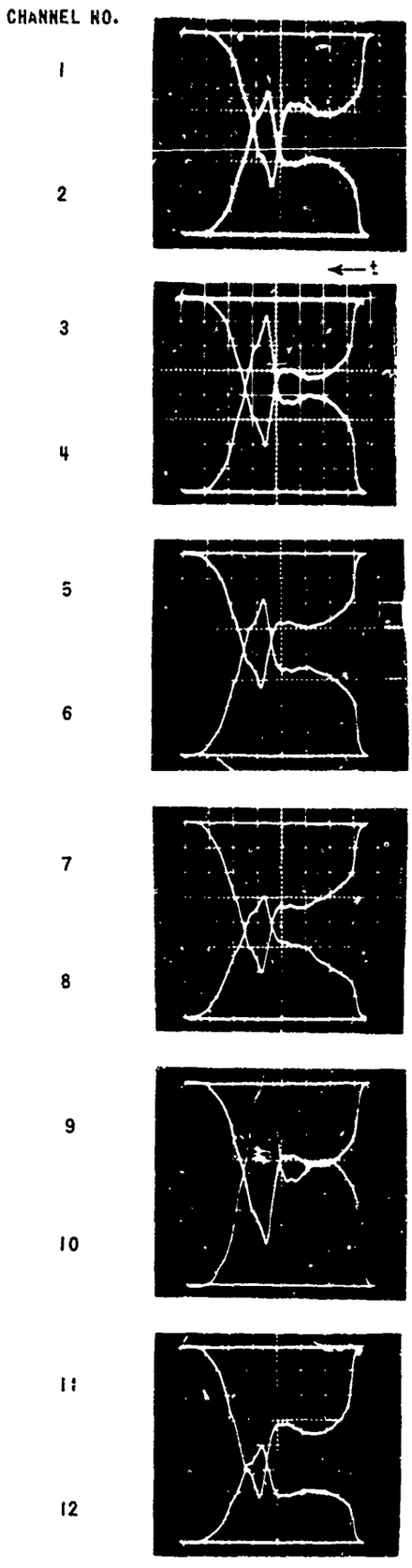


Figure 8 RADIATION PROFILES BEHIND A REFLECTED SHOCK WAVE IN NITROGEN

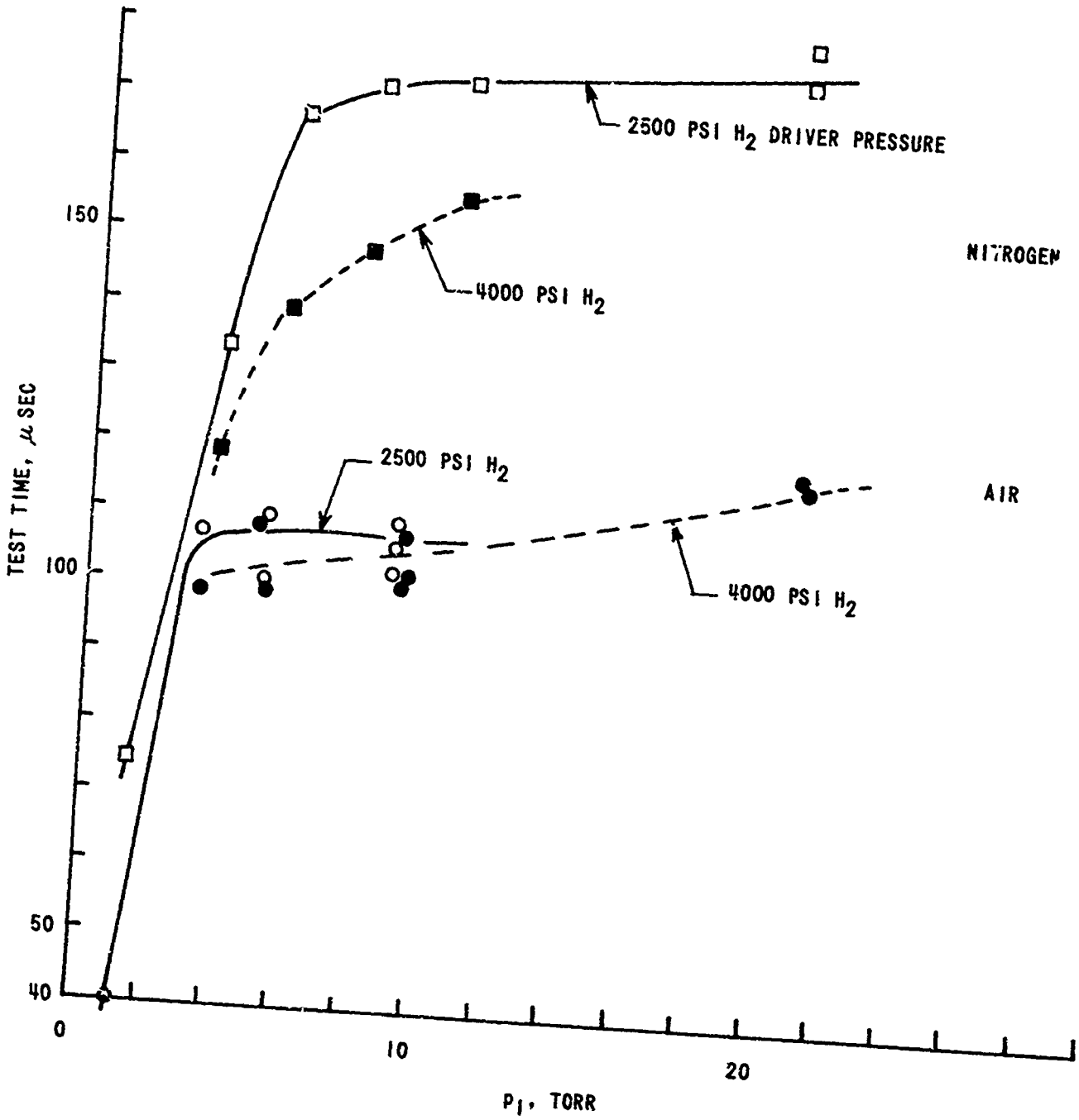


Figure 9 TEST TIME BEHIND REFLECTED SHOCK WAVES, 30 FEET FROM DIAPHRAGM

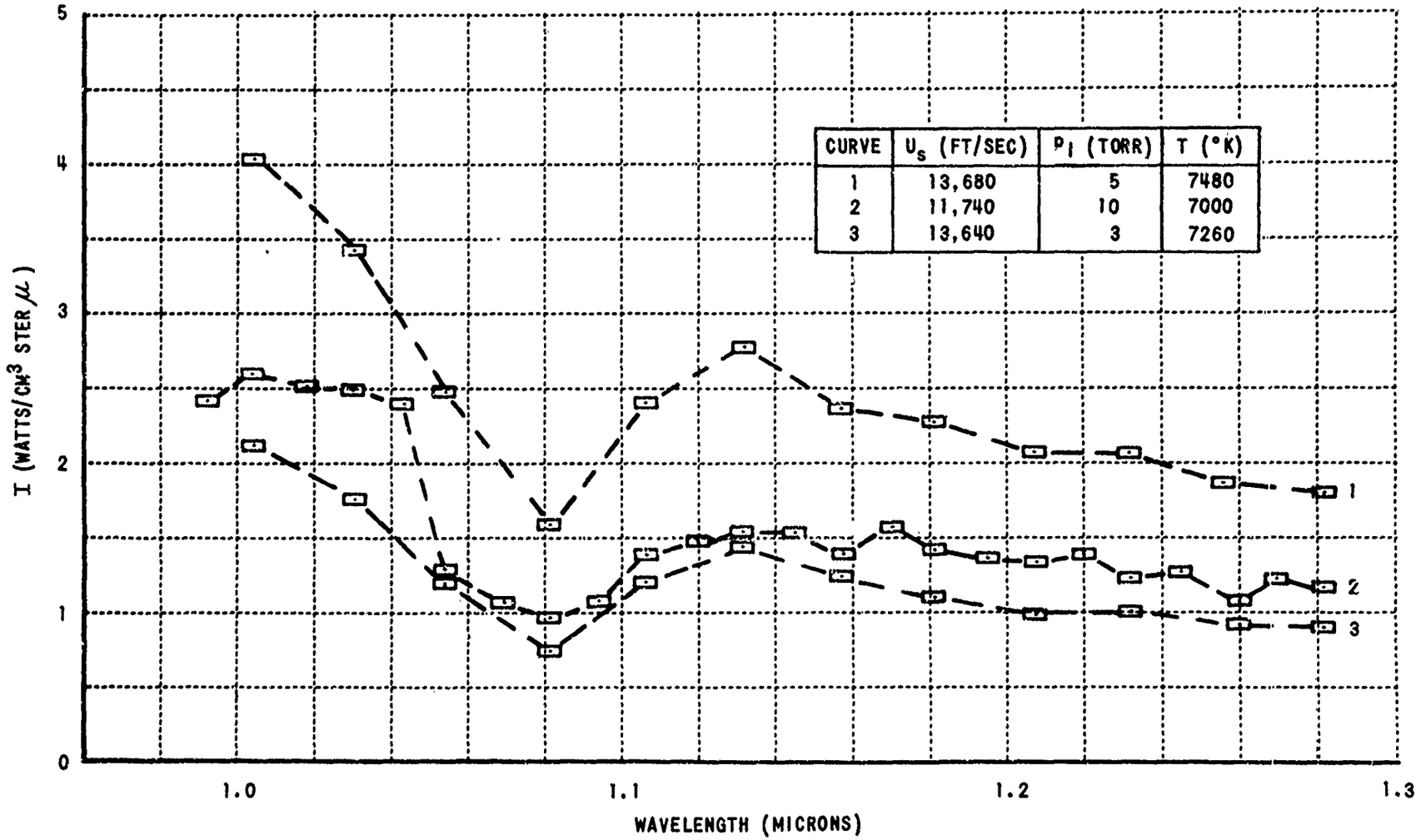


Figure 10 INFRARED SPECTRUM OF NITROGEN (REFLECTED SHOCK)

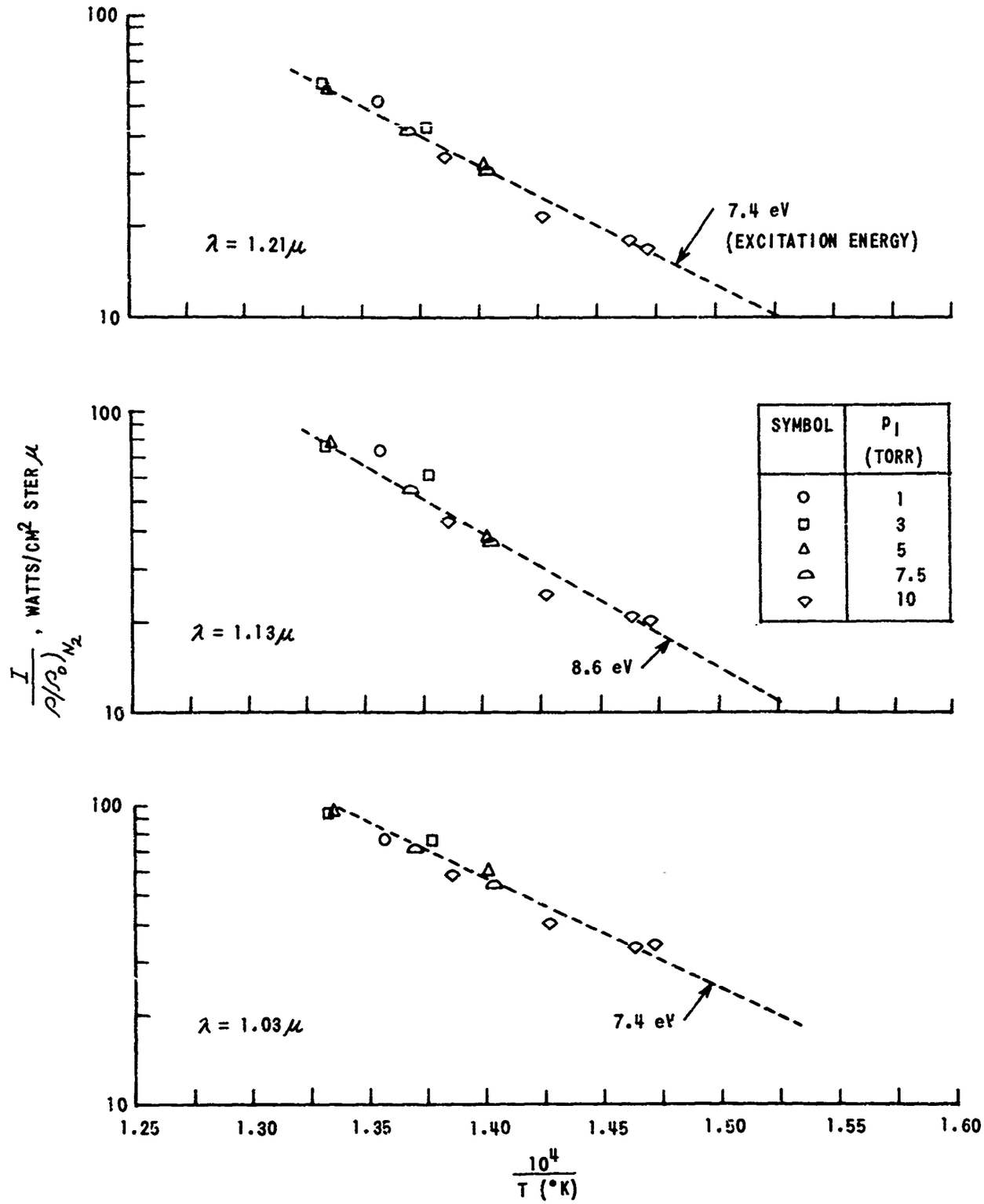


Figure 11 TEMPERATURE DEPENDENCE OF THE NITROGEN RADIATION (REFLECTED SHOCK)

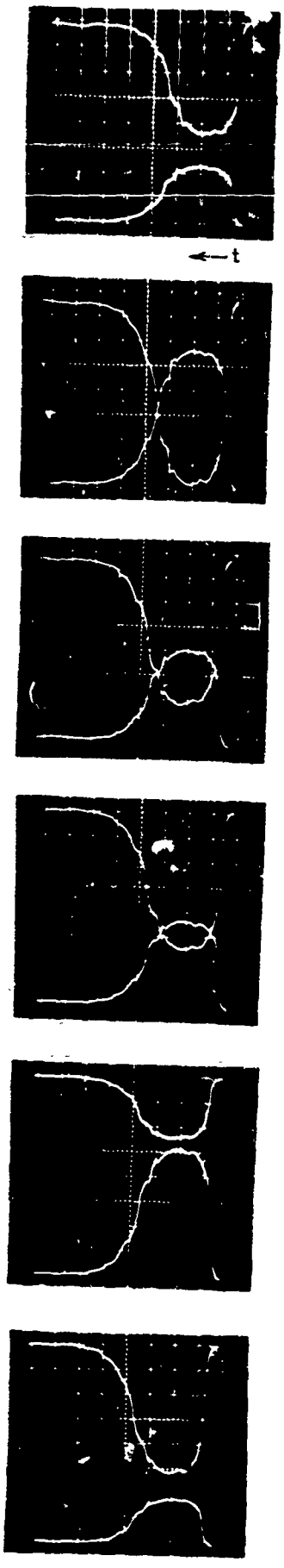


Figure 12 RADIATION PROFILES BEHIND A REFLECTED SHOCK WAVE IN AIR

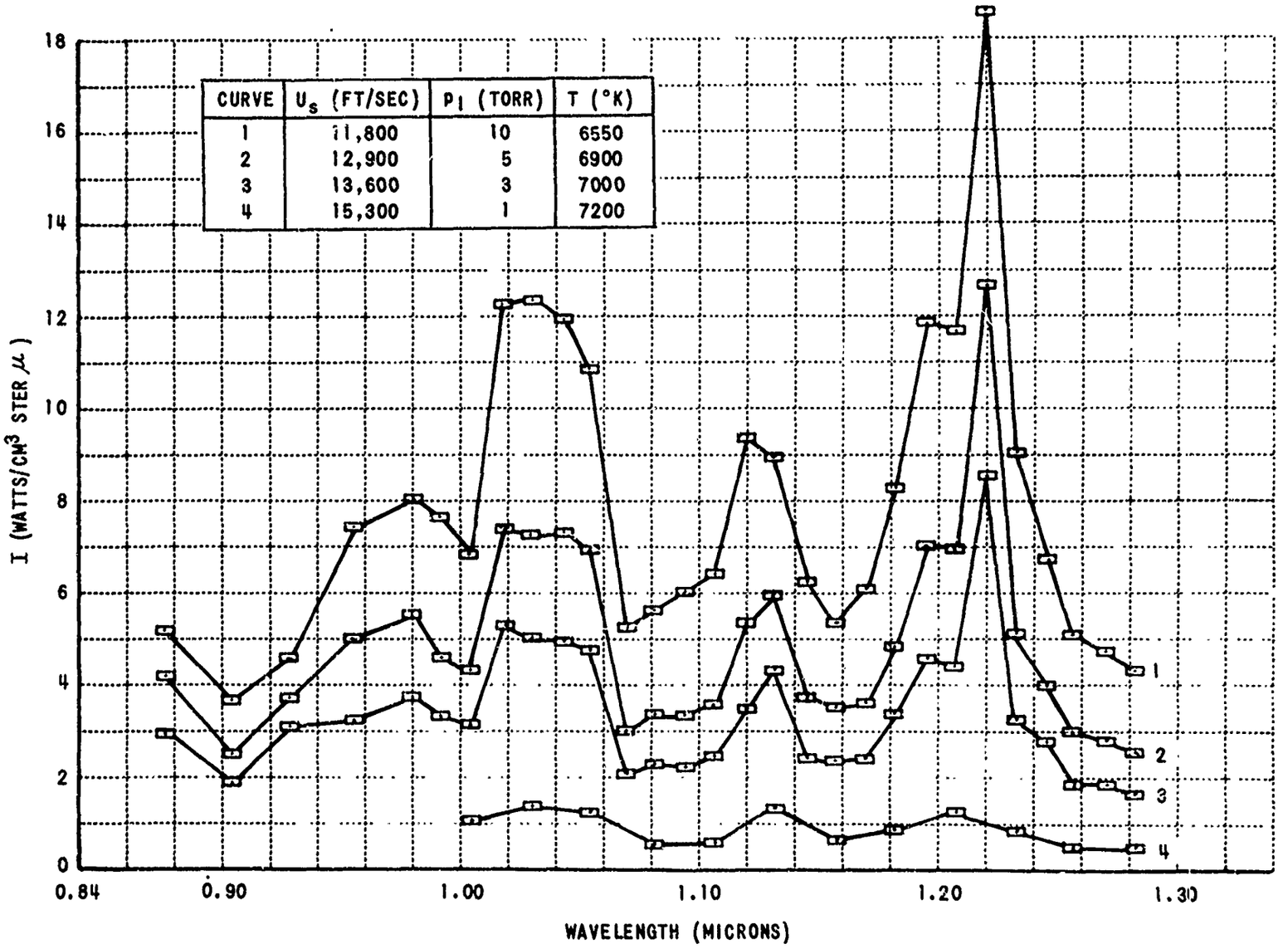


Figure 13 INFRARED SPECTRUM OF AIR (REFLECTED SHOCK)

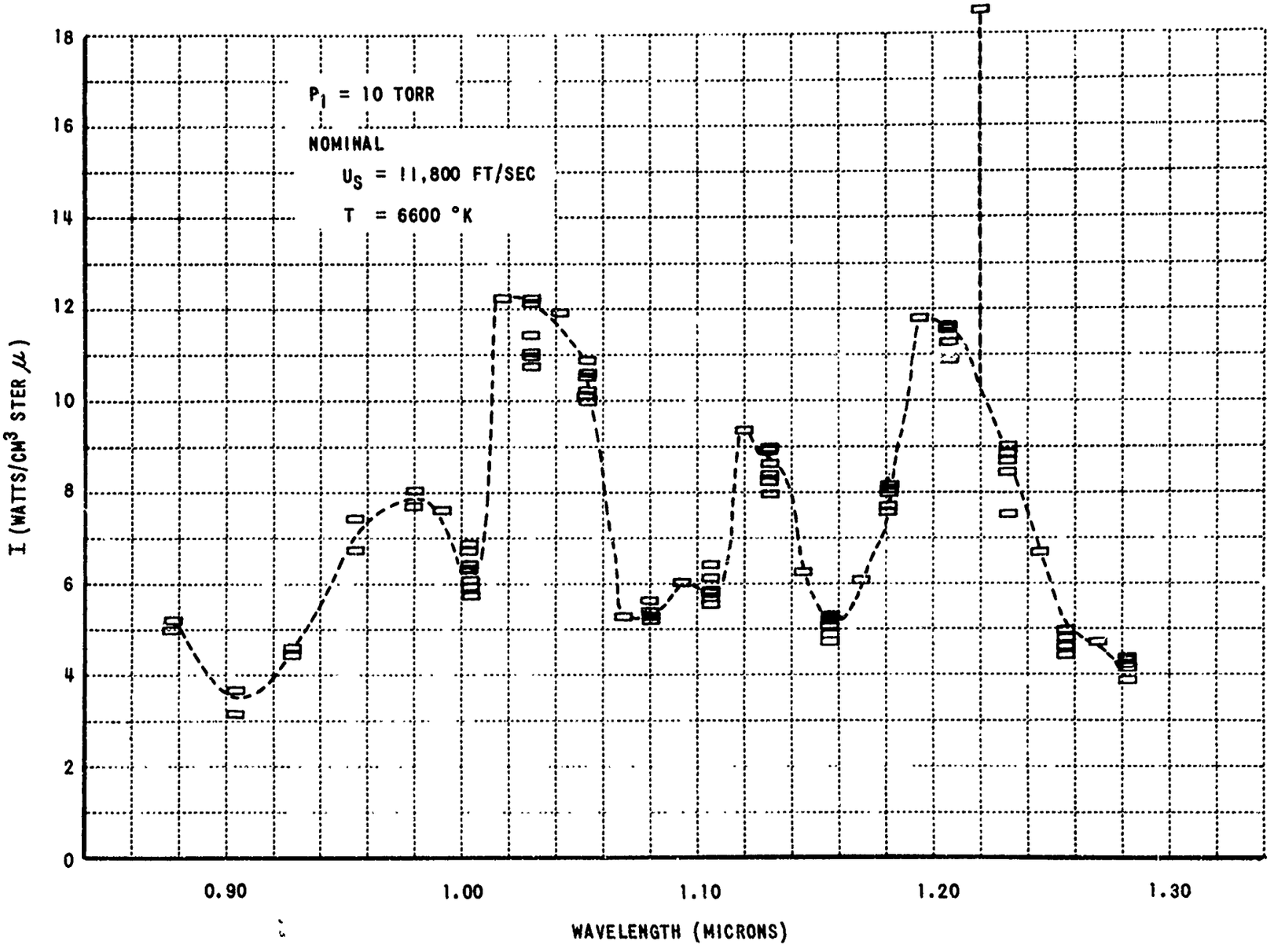


Figure 14 INFRARED SPECTRUM OF AIR SHOWING DATA SPREAD AT CONSTANT INITIAL CONDITIONS

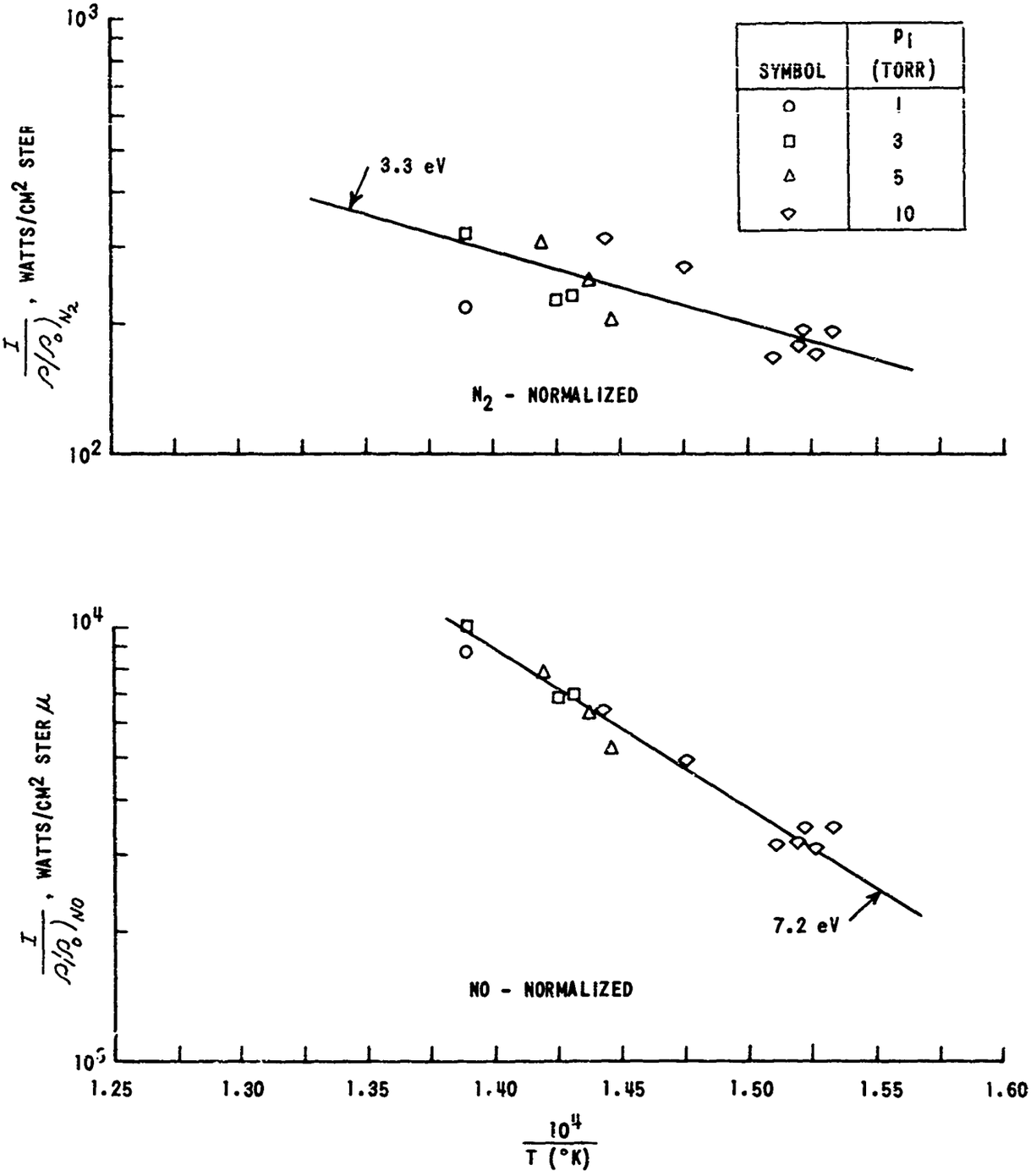


Figure 15 TEMPERATURE DEPENDENCE OF THE 1.03 μ RADIATION FROM AIR

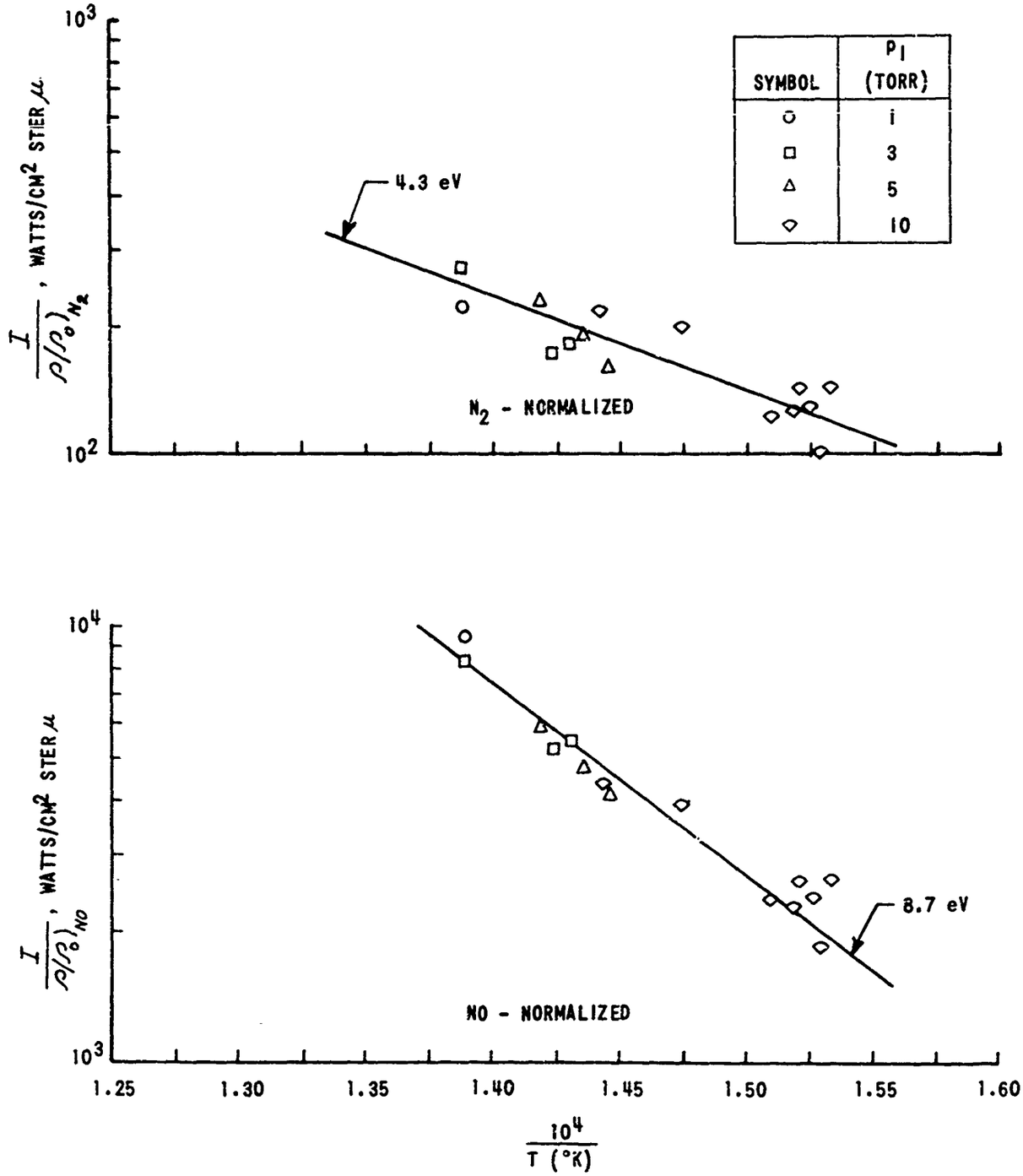


Figure 16 TEMPERATURE DEPENDENCE OF THE 1.13 μ RADIATION FROM AIR

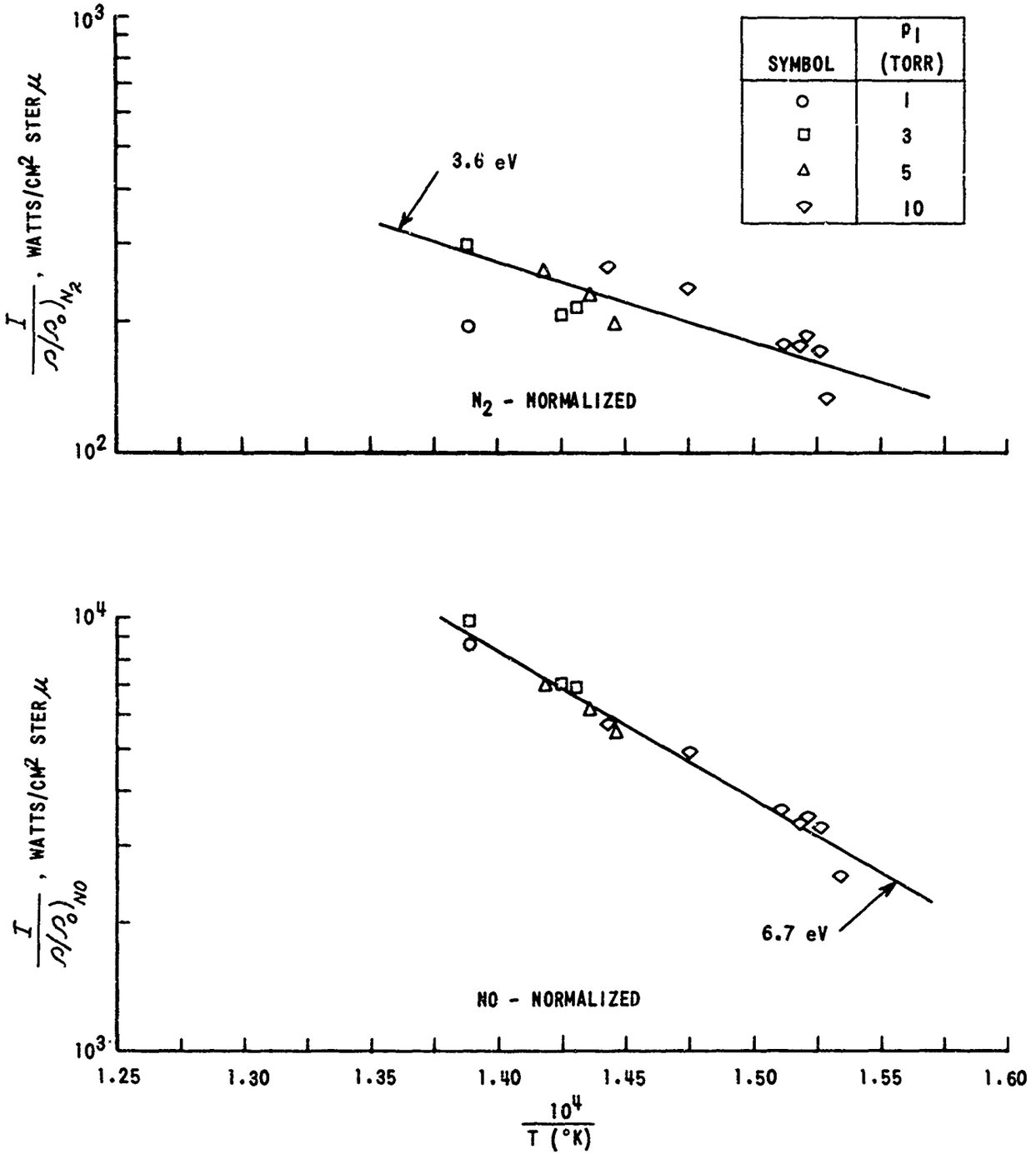


Figure 17 TEMPERATURE DEPENDENCE OF THE 1.21 μ RADIATION FROM AIR

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13 ABSTRACT

Quantitative spectroscopic measurements have been made of the infrared spectrum of shock-heated air and nitrogen between 0.9 and 1.3 micron. The measurements for air were obtained in the reflected shock region of a shock tube, covering the temperature range 6500-7200° K. The nitrogen data were obtained behind incident shock waves for temperatures between 4600-5700° K, and in the reflected shock region for temperatures from 6800-7500° K. In a previous study it was shown that air radiates much more significantly than nitrogen in this spectral range, and that the radiation could be attributed to transitions between excited electronic states of the nitric oxide molecule. The present measurements confirm these results and also show that the observed excitation energy of the radiation is inconsistent with the energy levels in nitrogen. The data from both studies are reviewed, and it is concluded that the NO hypothesis is consistent with the experimental evidence.

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